

Natural organic matter (NOM)-clay association in the Callovo-Oxfordian argillite and the Opalinus clay

T. Sch  fer, A. Bauer, F. Claret (Forschungszentrum Karlsruhe, INE), E. Ferrage, B. Lanson (Univ. J. Fourier, Grenoble)

Beamline(s): X1A

Introduction: Considered host rock types for the deep geological storage of nuclear waste include clay-rich formations as e.g. the Callovo-Oxfordian argillite (Bure, France) and the Opalinus shale (Z  rcher Weinland, Switzerland). The marine/terrestrial deposition of argillite and shale generally occurs in the presence of organic material and the P/T evolution during diagenesis and cata-/petrogenesis can change drastically the organic composition in these systems [1]. Reliable clay stability predictions can only be drawn if the NOM-clay association is precisely characterized. Therefore the clay fraction (< 2   m) of four Bure samples of borehole EST 104 and one Opalinus shale sample of borehole Benken were selected as representative of the whole sequence.

Methods and Materials: For details on clay fraction preparation and clay mineralogical characterization it is referred to [2, 3]. The TOC concentration in the Bure argillite is depth independent ~1.3 wt% and < 0.4 wt% in the Opalinus clay [2, 3]. In the NEXAFS spectra illite is identified using the X-ray absorption L-edge double feature at 297 eV and 300 eV of interlayer potassium. For C(1s) NEXAFS spectra deconvolution it is referred to [4].

Results & Discussion: The simultaneous measurement of the C(1s) NEXAFS and the potassium L-edge in the same pixel region clearly indicates an association of natural organic matter with K-rich clay phases (illite) in the Callovo-Oxfordian argillite (Fig. 1A). Furthermore no significant depth dependent C(1s) variations in the average spectra are noticeable after spectra deconvolution. The observed clay-NOM association might be interpreted by a so-called sorptive protection mechanism preventing diagenetic degradation of NOM via clay sorption [5]. The microscopy of the clay-NOM associates (Fig. 1B) shows a patchy blurred distribution [6]. The noted association implies that NOM sequestration may be more closely related to pattern of continental weathering and clay mineralogy [7]. In comparison, the untreated Opalinus clay (Fig. 1A) shows lower absorption on the potassium L-edges, therefore indicating a weaker association of NOM with K-rich illite. This might point to a preferential association with other clay mineral phases (kaolinite, chlorite) as indicated by additional FT-IR measurements [8]. Furthermore Opalinus clay is significantly depleted on aromatic functional groups. A possible explanation for the significant lower aromatic band intensities in the Opalinus shale might be the polycondensation associated relative increase of carboxyl and aliphatics according to the P/T history of the sediment.

References:

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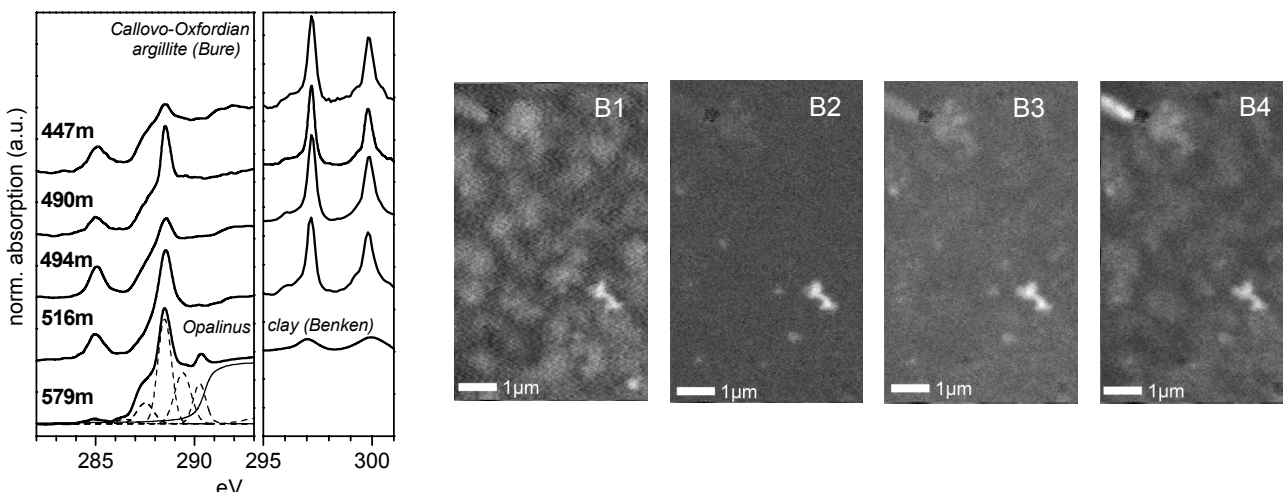


Figure 1: A1: C K-edge spectra of the Bure and Opalinus clay fraction and Gaussian deconvolution. A2: Potassium L_{2,3} edges of the samples. B: Ratio images ($-\log [I/I_0]$; $I_0 = \Sigma(280-283\text{eV})$) of sample 490m. B1: Potassium distribution, $I=297.2\text{eV}$; B2: aromatics, $I=285\text{eV}$; B3: aliphatics, $I=287.6\text{eV}$; B4: carboxyl, $I=288.4\text{eV}$.